OneNMR Probe 400-700 MHz

Technical Overview

Introduction

The OneNMR probe represents a new class of NMR probes. This technology is the most significant advance in solution-state probe technology in over a decade. The OneNMR probe is not a reworked version of a broadband or indirect detection probe, but a new technology free of the performance trade-offs of those classic designs. It is see an entirely new design with performance benefits unmatched by other probes.

Agilent Technologies

Sensitivity

The OneNMR probe is simultaneously optimized for both high- and low-band frequencies, and delivers the performance advantages of both the classic carbon probe and the highly sensitive proton probe in a single design. The signal/noise (S/N) specifications for the family of 400-700 MHz OneNMR probes is shown in Table 1, with excellent sensitivity on both channels.

It is understood that actual S/N performance will vary depending on how well your system is shimmed. The design and manufacturing of the OneNMR probe results in a very tight performance distribution so that all probes are very similar. The S/N results in Figure 2 were obtained using a typical 400 MHz OneNMR probe with an Agilent 400-MR magnet.

The proton sensitivity data in Figure 1 is 20 % greater than the specification. These data illustrate one of the dangers of comparing probes on the basis of published specifications alone. Probe specifications for a given vendor (probe to probe) tend to be consistent, making direct within-vendor comparisons easy. However, direct comparisons between vendors are much more difficult owing to differences in methods and philosophy. When sensitivity is used as a basis for probe selection, your safest bet is a direct head-to-head comparison with the same sample (yours) and operator (you).

Table 1. 400-700 MHz OneNMR Probe Sensitivity Specifications.

	400	500	600	700	Sample	Tube
^{1}H	480:1	730:1	900:1	1150:1	0.1 % Ethybenzene	Wilmad 545-pp
^{13}C	225:1	300:1	380:1	460:1	0.1 % Ethybenzene	Wilmad 545-pp
^{15}N	20:1	25:1	35:1	45:1	90 % Formamide	Wilmad 535-pp
^{31}P	90:1	135:1	170:1	220:1	0.0485 M TPP	Wilmad 535-pp
^{19}F	550:1	800:1	1050:1		0.05 % TFT	Wilmad 535-pp

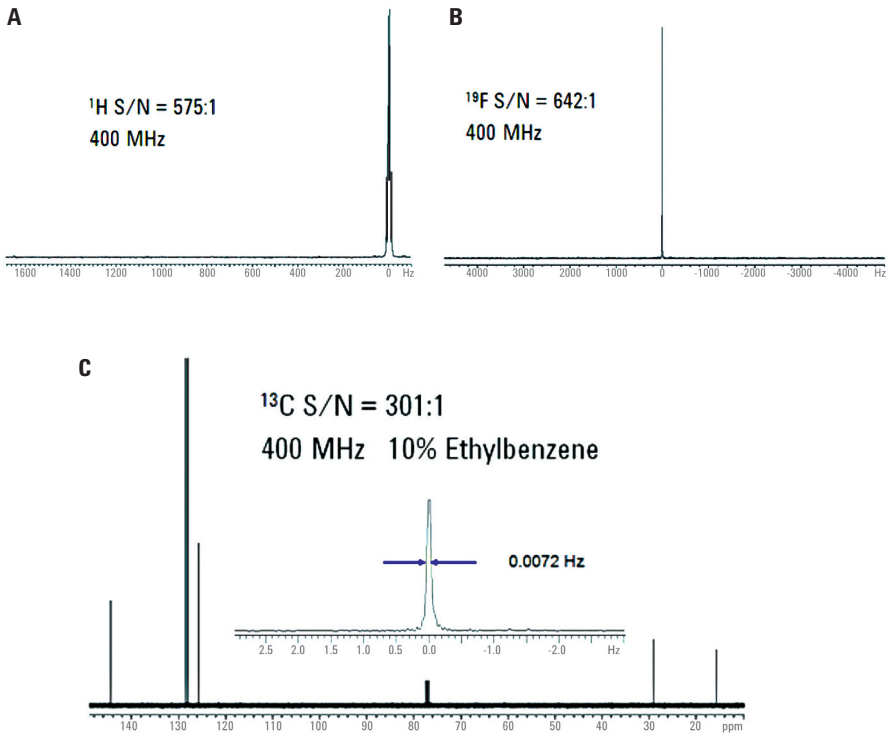

Figure 1. 400 MHz OneNMR Probe High & Low Band Sensitivity (A) Proton S/N, (B) Fluorine S/N, (C) Carbon S/N.

The OneNMR Probe lock sensitivity is also enhanced to provide a more stable lock and to support fast gradient shimming for increased flexibility (e.g. 3 mm tubes) and greater ease-of-use.

Sensitivity, while important, is just one aspect of probe performance and only part of the story. The sections which follow will introduce you to the advantages of the OneNMR probe that extend far beyond sensitivity alone.

400-700 MHz OneNMR Probe Lineshape Specifications

		Spinning		Non-spin
		^{13}C	^{1}H	^{1}H
50 %	≤	0.15	0.45	0.8
0.55 %	≤	1.5	5.0	7.0
0.11 %	≤	3.0	10.0	14.0
Sidebands	≤	1 %	1 %	

^{13}C Lineshape Decoupled Dioxane

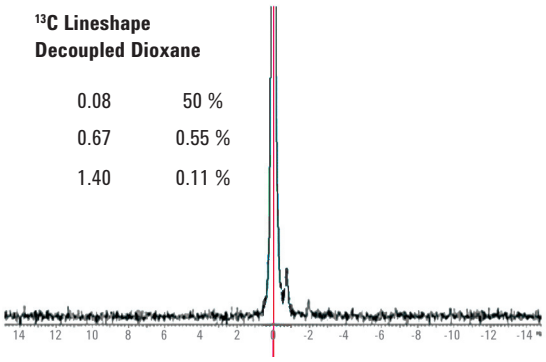

Figure 2. OneNMR Probe lineshape specifications (left) and a spinning ^{13}C dioxane example.

Pulse Performance and Lineshape

The 400-700 MHz OneNMR Probes provide superior lineshape both spinning and non-spinning which means ease of shimming and well resolved spectra. The lineshape specifications are shown in Figure 2, along with an example of the proton-decoupled ^{13}C NMR spectrum of dioxane.

The OneNMR probe's modern design and efficient power handling leads to excellent pulse performance. The PW90 pulse widths for the 400-700 MHz OneNMR probes are listed in Table 2. These relatively short PW90's are ideal for experiments requiring excitation or decoupling over a wide spectral window (e.g. ^{19}F).

Table 2. 400-700 OneNMR Probes pulse performance.

PW90	400 Mhz	500 MHz	600 MHz	700 Mhz	Sample
^{1}H	7 µsec	8 µsec	9 µsec	10 µsec	1 % ^{13}C-Iodomethane
^{13}C	8 µsec	10 µsec	9 µsec	10 µsec	1 % ^{13}C-Iodomethane
^{15}N	14 µsec	20 µsec	18 µsec	20 µsec	90 % Formamide
^{31}P	8 µsec	15 µsec	12 µsec	15 µsec	0.0485 M TPP
^{19}F	8 µsec	10 µsec	10 µsec		0.05 % TFT

RF Homogeneity

The OneNMR probe has excellent RF homogeneity on both channels while a dual broadband (DB) probe has relatively poor RF homogeneity. If you look at a spin projection comparing a standard dual broadband probe (Coil A) to the OneNMR Probe (Coil B), as shown in Figure 3, you can see that over the length of the sample, the amplitude of the signal with the OneNMR Probe is more uniform than for the standard dual broadband probe. What this means is that only the spins in the center of Coil A will be at maximum amplitude while nearly all the spins of Coil B will be at maximum amplitude. For a single pulse this difference may not be so important, but many experiments have several pulses in rapid succession. So if on the first pulse only 85 % of the spins line up, then on the second pulse only 85 % of 85 % line up, and so on until you very rapidly lose your signal. In contrast, with a more homogenous RF field, you lose less signal with each pulse and the summed signal from Coil B ends up being larger than Coil A. This is especially important when you consider that modern pulse sequences tend to incorporate more rather than fewer pulses.

The standard way to look at this is by comparing the ^{1}H 810 °/90 ° or the ^{13}C 720 °/0 °, where the higher ratio of intensities indicates better RF homogeneity. An average 810 °/90 ° for an indirect detection probe is around 70 % whereas a standard DB probe will give you around 55 %. When we initially introduced the OneNMR Probe, both the 810 °/90 ° and the 720 °/0 ° were 78 %, and the current release is even better. Consequently, not only is

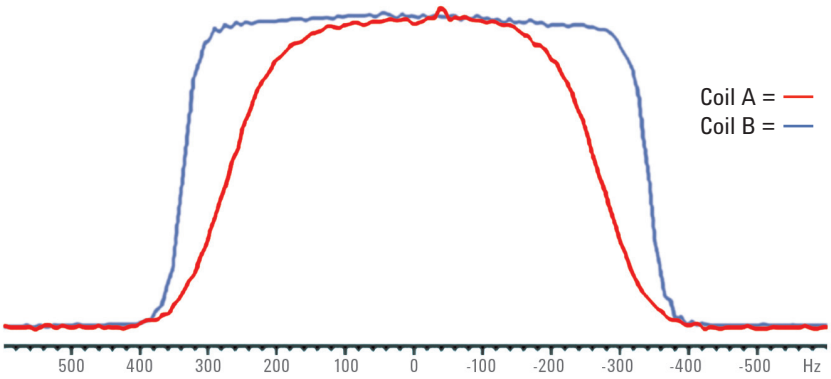

Figure 3. A comparison of spin projections (signal intensity along the z-axis of the coil) of a standard DB probe (Coil A, in red) and the OneNMR Probe (Coil B, in blue). The OneNMR Probe provides a more uniform signal than the standard DB probe.

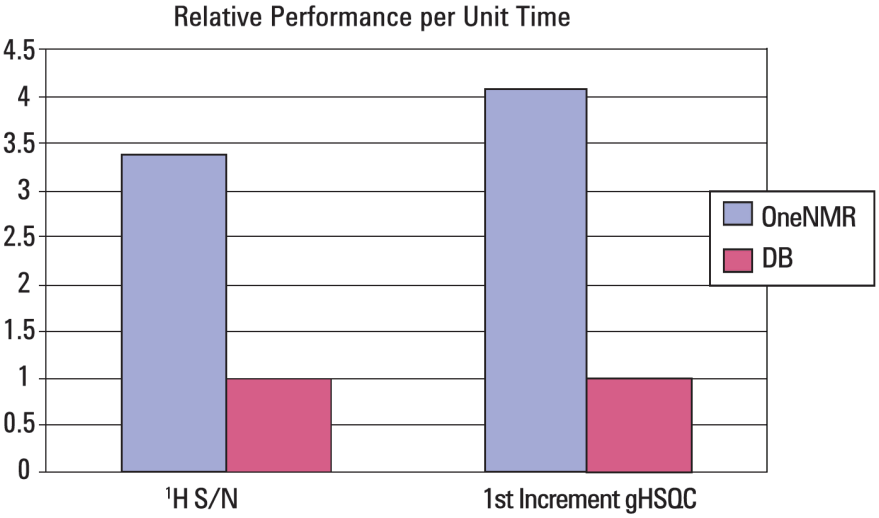

Figure 4. Relative performance of the OneNMR Probe compared to the standard DB probe. The results are given in units of time to complete the experiment.

the performance of the OneNMR Probe better than a standard DB probe in a 1D experiment, it is significantly better for 2D experiments as well.

The advantages of good RF homogeneity can be seen by comparing the OneNMR Probe to an indirect detection probe. The proton coil of the ID probe is closer to the sample and, as you would expect, this gives it a better signal-to-noise than the OneNMR Probe – 20 % better for a single 90 ° pulse. However the RF homogeneity (810 °/90 °) of the OneNMR probe is better than the indirect detection probe by about 9 %. This seemingly small difference in RF homogeneity has a big impact in 2D experiments with multiple pulses, such as the gHSQC-NOESY (Figure 4). The more homogenous RF field of the OneNMR probe compensates for the lower signal-to-noise ratio. This effect is

shown in Figure 5, where the OneNMR Probe (middle) performs almost as well as the indirect detection probe (right) in this 2D experiment. For comparison, the performance of a DB probe (left) is also shown.

Superior Decoupling

When you combine the efficient power handling, pulse performance, and RF homogeneity of the OneNMR probe, the result is outstanding decoupling performance. In real-world applications, like a ^{13}C observe experiment, improved decoupling results in narrower lines (increased resolution) and increased sensitivity. The improved decoupling can be seen by comparing the line-widths of the OneNMR and Dual Broadband probes under identical conditions (see Figure 6).

Superior decoupling leads directly to increased sensitivity. The 500 MHz 1D carbon spectra for vitamin B12 were measured under identical conditions using the ID, DB, and OneNMR probes. The results (Figure 7) show significant sensitivity enhancements for many peaks when using the OneNMR probes. You would not have predicted this outcome on the basis of carbon sensitivity alone, since the Dual Broadband has a slight advantage. Once again we see that sensitivity, while important, isn't the whole story.

Because decoupling efficiency is such an important factor in ^{13}C performance, it is desirable to include it in any sensitivity testing. For this reason, we find 10 % ethylbenzene a superior (real-world) ^{13}C sensitivity test since it is measured under proton-decoupled conditions. The ASTM standard, while important for its historical significance, was developed for use when decoupling efficiency was poor. Since modern NMR spectrometers exhibit excellent decoupling, the ASTM standard is no longer relevant.

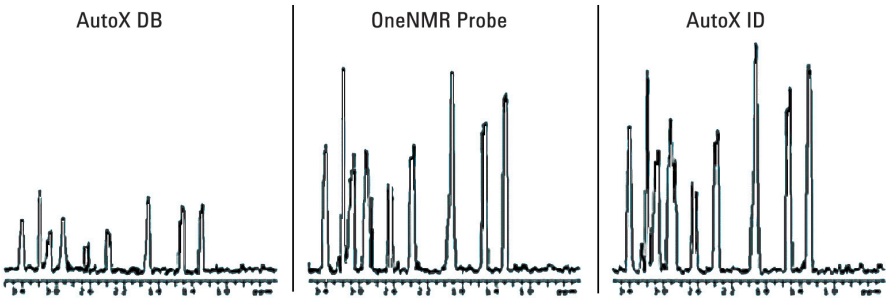

Figure 5. OneNMR Probe advantage in 2D experiments. Three gHSQC-NOESY spectra are identically scaled using the AutoX DB Probe (left), the OneNMR Probe (middle), and the AutoX ID Probe (right). The superior RF homogeneity of the OneNMR probe compensates for the ID probe's greater sensitivity (20 %) to yield comparable results.

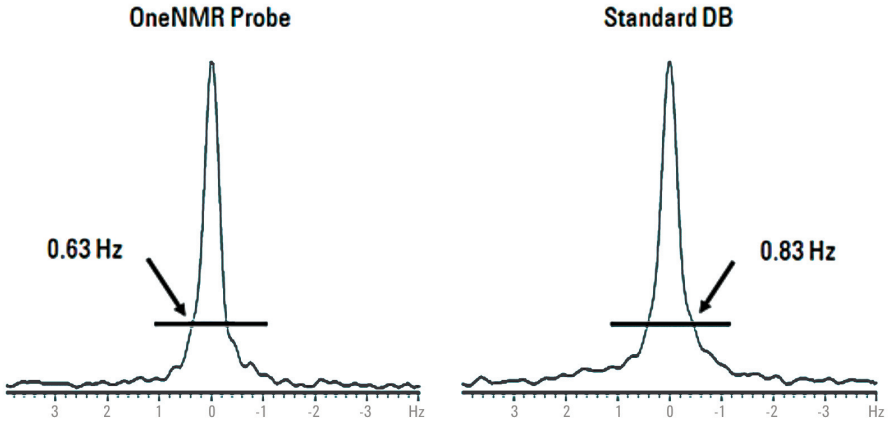

Figure 6. Decoupled Cholesteryl Acetate (28 ppm) resonance at 400 MHz, comparing the 20 % line-width of the (a) OneNMR Probe and (b) Dual Broadband Probe.

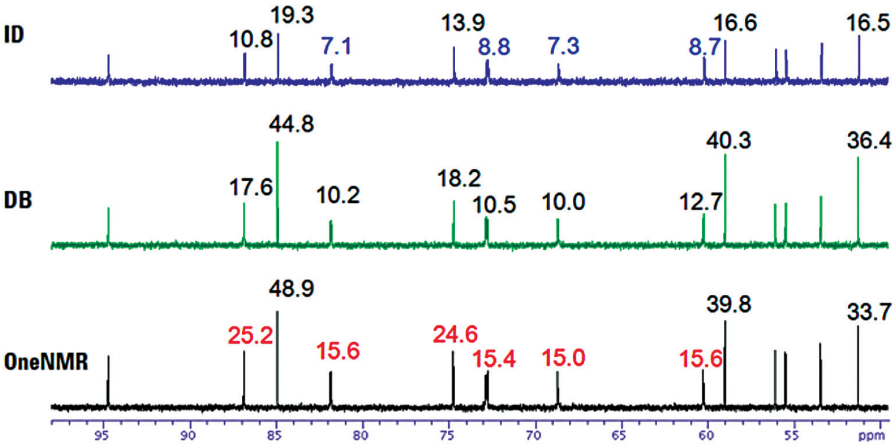

Figure 7. Decoupled 500 MHz 1D Carbon spectra for vitamin B12 collected using an ID probe (top), DB probe (middle) and OneNMR probe (bottom).

Water Suppression

The OneNMR probe's excellent sensitivity, pulse performance, and RF homogeneity make it an ideal probe for water suppression. The 400 MHz presaturation spectrum of 2 mM sucrose (90:10 H_2O/D_2O) shows a 65 Hz residual water peak and an anomeric splitting of 85 % (Figure 8). The right-hand spectrum was acquired under automation using PURGE and 8 scans. These results show that the OneNMR probe has outstanding performance in water suppression.

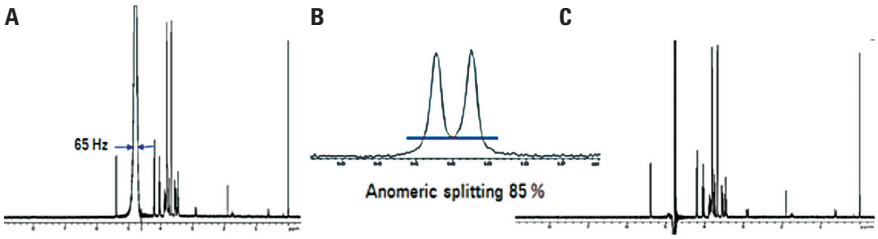

Figure 8. 2 mM sucrose (90:10 H_2O/D_2O) at 400 MHz: presaturation water suppression (A), anomeric splitting (B), and PURGE (C)water suppression, acquired under automation.

Salt Tolerance

NMR samples interact electromagnetically with the RF coils in the NMR probe. The magnitude of this interaction is proportional to the dielectric constant of the sample. When placed in the probe, samples with a high dielectric constant (e.g., ionic solutions) couple strongly to the RF coils, increasing the capacitance of the circuit and changing the tuning of the probe. Unless the probe is re-tuned for this new condition, the length of the 90 ° pulse width can suffer dramatically. Conversely, a probe tuned appropriately for a high dielectric sample will not perform as well if the sample has a comparatively low dielectric constant (e.g., chloroform).

The performance cost for running the NMR system in a poorly tuned state is significant for most standard probes, but this is not the case for the OneNMR Probe. The unique design of the OneNMR probe is very tolerant of dielectric differences, thereby eliminating the need for sample tuning for routine ^{1}H and ^{13}C studies.

A	Dual Broadband	
	PW90	S/N
Tuned to chloroform	10.75 µs	1.00
Tuned to 200 mM salt	15.00 µs	0.59

B	OneNMR	
	PW90	S/N
Tuned to chloroform	6.95 µs	1.00
Tuned to 200 mM salt	7.55 µs	0.94

Figure 9. Relative ^{13}C probe performance for a chloroform sample when tuned to chloroform and 200 mM salt for the (A) 500 MHz Dual Broadband Probe, and the (B) 500 MHz OneNMR Probe. Both signal-to-noise measurements were made using the pulse width and power levels calibrated for the accurately tuned sample.

This feature allows high-quality data collection on typical organic chemistry samples without the cost in time, wear and tear, and complexity required to actively tune the probe for each sample.

To demonstrate this effect, a standard 500 MHz, 5 mm DB probe was accurately tuned on an organic chemistry sample dissolved in deuterochloroform. Carbon spectra were acquired to establish baseline performance for the 90 ° pulse width and sensitivity. An aqueous 200 mM NaCl sample was then inserted into the probe and the system was tuned to this sample. Using this tune setting, the chloroform sample was returned to the magnet, and the pulse width and sensitivity data were once again collected. The results (Figure 9) show that a classic DB probe suffers a significant loss in sensitivity (39 %) and pulse performance under these conditions. Repeating the experiment with the OneNMR probe shows it to be remarkably tolerant of these high salt conditions retaining 94 % of its sensitivity with a much smaller impact on pulse width.

Given the ^{13}C performance results presented above and the excellent ^{1}H specifications of the OneNMR probe, one might anticipate that the proton channel would suffer from this type of intentionally mis-optimized tune experiment. This is not the case. When the same worst-case set of tuning experiments were repeated using the high frequency channel on the 500 MHz OneNMR probe, the performance changes between the well-tuned probe and the poorly tuned probe were negligible. The proton 90 ° pulse width increased by 5.9 %, while the S/N ratio decreased by only 5.3 %.

The HSQC experiment is a cornerstone NMR experiment for organic chemistry. It is also one of the more challenging experiments with respect to the quality of the NMR pulses used to collect the data. This makes it a perfect test experiment to demonstrate the ability of the OneNMR probe to yield high-quality data without the need for careful tuning adjustments.

Figure 10 displays two gHSQC data sets obtained on a mixture of two alkaloids in deuterochloroform using the 500 MHz OneNMR probe. These data show that running a demanding 2D experiment without tune optimization has little effect on sensitivity. In fact, comparison of the first increment of two adiabatic HSQC experiments with the probe tuned, versus detuned as described above, yielded a S/N change of less than 9 %.

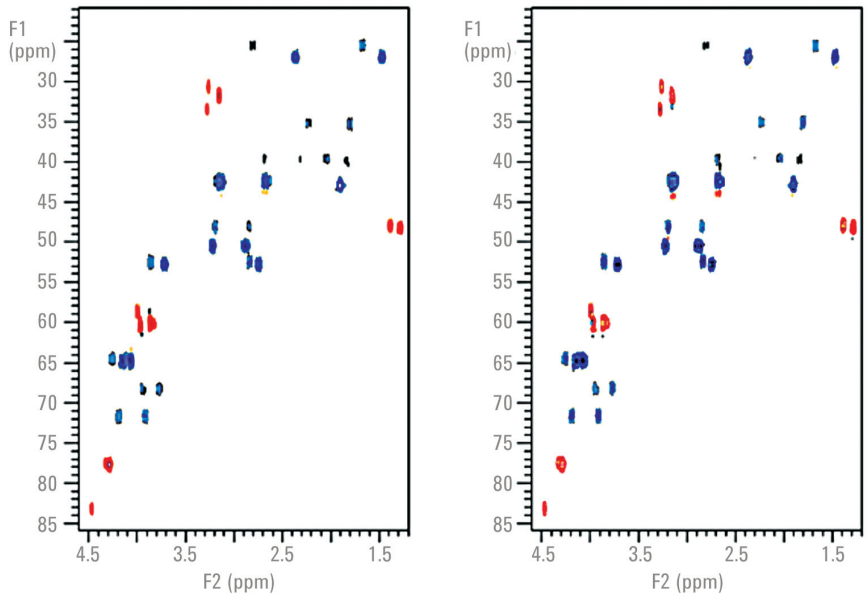

Figure 10. gHSQC data spectra acquired on a mixture of two alkaloids in deuterochloroform using the OneNMR probe. The data in the left panel were obtained with the RF coils carefully tuned to the sample. The data in the right panel were obtained on the same sample but with both the proton and carbon RF coils tuned on a sample of 200 mM NaCl in D_2O. No attempt was made to compensate for the mis-optimization of the RF pulses in the second experiment; the pulse widths, power levels, and parameterization used for each experiment were identical, and displayed at the same absolute contour level. The experiment time for each data set was less than 5 minutes.

Solvent Tuning Tolerance

The ability of the OneNMR probe to accept a wide range of solvents with minimal change in probe tuning means that, for routine organic chemistry applications, the OneNMR probe can be used to collect high-quality data without adjusting the tuning circuit from sample-to-sample.

The typical NMR solvents used in organic chemistry do not represent a large range of dielectric constants: benzene (ϵ_0 2.27) is at the low end of the scale and water (ϵ_0 80.1) is at the high end. Given this situation, one could easily tune the OneNMR probe to the middle of your working range and simply leave it there. The full range of organic NMR solvents would then be available for use without any need to retune the probe, while maintaining essentially all of the excellent performance of the OneNMR probe. This is especially useful for high throughput applications.

Automatic Probe Tuning – ProTune

ProTune is an advanced system for automatic probe tuning and matching which includes accessory hardware and software components built into Agilent VnmrJ software.

ProbeID

ProbeID is a new feature which allows the console and software to recognize and communicate directly with the probe. Building this intelligence into the probe allows you to work more intuitively while the system does the heavy lifting. Benefits of ProbeID include ensuring that various operational parameters remain within the limits of the probe (such as RF power and temperature). The software can prevent the accidental selection of incompatible probe files, which can be helpful in automation and multi-user environments.

ProbeID allows the factory to store probe specifications, calibrations, and probe-test data directly on the probe itself. The probe will contain a copy of the factory and installation test data, tuning data, and probe files should they ever be needed for reference or service. With ProbeID, probe-specific data always remains with the probe.

Summary

The OneNMR probe represents an entirely new class of NMR probes, unlike the classic broadband or indirect detection probes available today. The OneNMR probe has excellent sensitivity on both channels, but this is just a small part of the performance capabilities. The probe exhibits excellent RF-homogeneity on both channels, excellent lineshape and pulse performance, superior decoupling, enhanced lock sensitivity, and unprecedented salt and solvent tuning tolerance. The performance benefits of the OneNMR probe are unmatched by any other probe.

Learn more
www.agilent.com/chem/nmr

Find a local Agilent customer center
www.agilent.com/chem/contactus

USA and Canada
1-800-227-9770
agilent_inquiries@agilent.com

Europe
info_agilent@agilent.com

Asia Pacific
inquiry_lsca@agilent.com

This information is subject to change without notice.

© Agilent Technologies, Inc., 2012

Printed in the USA, March 30, 2012
5990-7612EN

Agilent Technologies